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EDLC electrodes from cellulose-based carbon aerogels: influence of the carbon surface chemistry

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Abstract. This work investigates the influence of the carbon surface chemistry on the carbon's electrochemical performance if used as EDLC electrode material. Carbon aerogels were synthesized by crosslinking cellulose acetate through a non-toxic isocyanate and subsequent drying in supercritical CO₂ and pyrolysis in inert atmosphere (1000°C, nitrogen atmosphere). Subsequently, the surface chemistry of the carbon aerogels was modified by oxidation (in H₂O₂) or by nitrogen introduction (impregnation with melamine and co-pyrolysis). Thus the carbon material's surface chemistry was modified depending on the modification method, while the morphology remained similar. All carbon samples were analyzed in terms of morphology (by nitrogen adsorption and mercury porosimetry), composition (elemental analysis), and surface chemistry (Boehm titration and pH_{PZC}). For electrochemical analysis, carbon aerogels were tested in the form of EDLC electrodes in a symmetric test assembly in aqueous electrolyte (cyclic voltammetry and galvanostatic cycling). Results show that the carbon's capacitance can be increased by the introduction of heteroatoms. However, the type of functional groups present on the carbon surface seems to really determine capacitance as opposed to the mere presence of oxygen or nitrogen atoms.

1. Introduction

Our society's steadily growing dependency on fossil energy sources hazards reliable energy supply in the future. Energy efficiency, counteracting this risk, can be drastically augmented by efficient storage of surplus energy. Electrical double layer capacitors (EDLCs) store electrical energy directly in electrostatic interactions, i.e. not forcing electrical energy to undergo any energy conversion process leading to a loss of reconvertible energy. One crucial element of EDLCs, significantly determining the capacitance and resistance and therefore also the energy and power capabilities, are their electrodes generally consisting of nanostructured carbon material.

Carbon aerogels, e.g. resulting from the pyrolysis of resorcinol-formaldehyde organic aerogels first developed by Pekala in 1989 [1], are widely recognized as interesting material for EDLC electrodes. This is due to the fact that their nanostructure can be tailored to fulfil the morphological requirements of an application via soft chemistry, i.e. the sol-gel process. An obvious disadvantage of most well-known organic aerogels is the utilisation of mostly harmful precursors. To avoid the utilisation of toxic substances and to valorise renewable resources at the same time, we developed a novel organic aerogel on the basis of cellulose acetate crosslinked through a non-toxic isocyanate [2]. Pyrolysis in inert atmosphere (1000°C, nitrogen atmosphere) transforms the organic aerogel into a carbon aerogel.

Numerous studies have been carried out correlating carbon morphology with its influence on the electrochemical performance of the carbon material as EDLC electrode. Highest capacitance values were found to be achieved by using carbon material with high microporous volumes [3, 4] and very narrow pore size distributions of 0.7-0.8 nm, depending on the electrolyte [5, 6]. Simultaneously, the composition and in some cases the surface chemistry have been found to also influence the carbon capacitance. Carbon-based EDLCs have long been known to exhibit a small part (1-5%) of their capacitance as pseudocapacitance due to the faradaic reactivity of surface oxygen-functionalities [7]. Capacitance-enhancing effects were also observed for nitrogen-containing carbons [8, 9, 10]. This work therefore aims at clarifying the influence of the composition and the surface chemistry on the carbons' capacitance and on its electrochemical performance in general.

2. Experimental Methods

2.1. Carbon aerogel synthesis

Carbon aerogels were prepared by pyrolysis of supercritically dried cellulose-acetate-based organic aerogels. Cellulose-acetate-based organic aerogels were synthesized by sol-gel method, according to the protocol established by Fischer et al [2].

Cellulose acetate (acetyl content of 39.8 wt. %, number-average molecular weight M_n of 30 000, Sigma-Aldrich) was crosslinked by PMDI (polymethylene polyphenylpolyisocyanate, 31.8 wt% NCO content, Lupranat® M20S, BASF) in extra-dry acetone (purity of 99.8 %, Sigma-Aldrich) acting as reaction medium. The step-growth polymerisation, i.e. the crosslinking reaction consisting of the formation of urethane bonds between the cellulose acetate's free hydroxyl groups and the PMDI's isocyanate groups, was catalyzed by the amino compound DABCO® TMR (1,4-diazabicyclo[2.2.2]octane, Air Products).

For the sol-gel synthesis cellulose acetate was added to acetone (10 wt% cellulose acetate) and mechanically stirred for 24 hours at room temperature, in order to obtain a translucent homogeneous polymer dispersion. The catalyst (0.25 g/l_{Acetone}) and diisocyanate crosslinker PMDI (20 wt% of cellulose acetate) were each dissolved separately in acetone under mechanical stirring for 10 minutes. In a first step the catalyst sol was added to the cellulose acetate solution and stirred again for 10 min. In a second step, the PMDI sol was added to the cellulose acetate/catalyst solution under mechanical stirring. Gels were aged for 7 days at room temperature, to complete syneresis.

Supercritical drying of the acetate cellulose based gels was performed in a 1-litre autoclave. The gels impregnated by acetone were washed in supercritical carbon dioxide (5 kgCO₂/h) at 85 bar and 40°C for 4 hours. After having recovered the interstitial liquid phase, CO₂ was vented out isothermally (0.08 bar/min, 40 °C) to prevent any tensile stress and condensation phenomena to occur.

Organic aerogels were pyrolyzed in nitrogen atmosphere (under a continuous flow of nitrogen of 3 l/h). The samples were heated at 4 °C/min to a maximum pyrolysis temperature of 1000 °C, at which they dwelled for one hour. Cooling, still under nitrogen flow, was left to thermal inertia.

2.2. Chemical modifications of the carbon aerogel

Oxidized samples were prepared by the reaction of the initial cellulose-acetate-based carbon aerogel powder with a solution of 5 N H₂O₂. The carbon/acid solution-mixture was continuously stirred for 48 hours at ambient temperature. Samples were washed with distilled water until no change in the pH was detected anymore. The resulting carbon was dried overnight at 120 °C. In the following, the oxidised carbon is referred to as CA-OX. Functionalisation of the initial carbon aerogel powder with nitrogen was performed by impregnation and co-pyrolysis with melamine (sample CA-M). To this aim, the carbon aerogel (9 g) was mixed with a melamine suspension (6 g of melamine in 50 mL of ethanol) and stirred at room temperature for 5 h. Subsequently, the carbon/melamine mixture was treated at 750 °C (dwelling time 1 hour) in nitrogen. This functionalisation procedure is based on a work by Seredych et al. [10]. The initial, untreated carbon aerogel is referred to as CA hereafter.

2.3. Characterization methods

The morphology of the carbon powders was analyzed by low temperature nitrogen adsorption and mercury porosimetry. Nitrogen sorption isotherms were measured at 77 K with a Fisons Sorptomatic 1990 after outgassing at 10⁻³ Pa for 24 h at ambient temperature. From the nitrogen adsorption isotherms, we determined the BET specific surface area, S_{BET} , the micropore volume by the Dubinin–Radushkevich equation, V_{DUB} , the cumulative volume of pores of width between 2 and 7.5 nm by the Broekhoff–de Boer theory, and the pore volume calculated from the adsorbed volume at saturation, V_p . V_p corresponds here to the total porous volume,

as the samples do not feature any macroporosity unmeasurable by nitrogen adsorption. Mercury porosimetry measurements were performed with a Pascal porosimeter thermoelectron and provided the pore volume corresponding to pores >7.5 nm, V_{Hg} . Additionally, the skeletal density, ρ_s , was determined by helium pycnometry, with a Micromeritics Accupyc 1330 pycnometer, and the bulk density, ρ_{bulk} , was calculated according to $\rho_{bulk} = 1/[V_p + (1/\rho_s)]$.

Carbon, hydrogen, nitrogen, and sulphur contents were determined by elemental analysis at the Central Analysis Service of the CNRS (Vernaison, France). Before analysis, all samples were dried for one hour in air at 120 °C.

The surface chemistry of the carbon aerogels was characterized by the Boehm method and the measurement of the pH of the point of zero charge measurement (pH_{PZC}). Concentrations of acidic and basic surface groups were determined according to the Boehm method [11]. To this aim, 0.5 g of carbon was suspended in 25 mL of a 0.05 N solution of sodium hydroxide or hydrochloric acid. The vials were sealed and the solutions stirred for 24 h. Then 8 mL of each filtrate was pipetted and the excess of base or acid was titrated with HCl or NaOH. The quantity of all acidic sites was calculated under the assumption that NaOH neutralizes carboxyl, phenolic and lactonic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid that reacted with the carbon.

To measure the pH_{PZC} , 0.5 g of carbon was added to 10 cm³ of CO₂-free distilled water and the suspension was stirred for 24 h to reach equilibrium. The final pH of the suspension was taken as the pH_{PZC} of the carbon [12].

Electrochemical analysis was investigated in acid aqueous electrolyte (1 M H₂SO₄) in a two-electrode test cell. Electrochemical performance was analyzed using a potentiostat/galvanostat BioLogic HCP-803 for cyclic voltammetry and galvanostatic charge/discharge measurements. EDLC electrodes were prepared by mixing carbon aerogel powder and PTFE (polytetrafluoroethylene 60 wt.%, Sigma Aldrich) in a mass ratio of 9:1. For better homogenization, the carbon/PTFE-mixture was fluidized by ethanol (purity of at least 99.8%, Sigma Aldrich). Electrodes were given a thickness of 300 μ m.

3. Results and Discussion

3.1. Morphology

The morphologies of the initial carbon sample CA and the modified samples CA-OX and CA-M are rather similar. The specific surface area for CA-M is slightly lower in the case of the oxidized and the initial sample. A small part of the CA-M sample's porosity might be blocked by nitrogen containing functional groups on the carbon surface. Microporous volumes, considered the most important parameter for EDLC performance [3, 4], are evidently also slightly smaller for CA-M as compared to CA. However, values for microporous volumes are roughly of the same order of magnitude. Initial cellulose-acetate-based carbon aerogel CA features slightly lower densities and marginally higher overall porous volumes. Mean pore size as determined from nitrogen sorption isotherms remains constant for all samples around 10 nm.

Table 1. Specific surface area S_{BET} , micropore volume V_{DUB} , cumulative volume of pores between 2 and 7.5 nm $V_{2-7.5}$, total porous volume V_p , volume corresponding to pores >7.5 nm V_{Hg} , skeletal density ρ_s , and bulk density ρ_{bulk} for initial (CA) and modified carbon aerogels (CA-OX, CA-M)

| Sample | S_{BET} (m ² /g) | V_{DUB} (cm ³ /g) | $V_{2-7.5}$ (cm ³ /g) | V_p (cm ³ /g) | ρ_s (g/cm ³) | ρ_{bulk} (g/cm ³) |
|--------|----------------------------------|-----------------------------------|-------------------------------------|-------------------------------|----------------------------------|---------------------------------------|
| CA | 165 | 0.07 | 0.28 | 0.35 | 1.92 | 1.15 |
| CA-OX | 152 | 0.06 | 0.24 | 0.30 | 2.06 | 1.23 |
| CA-M | 130 | 0.06 | 0.23 | 0.29 | 2.07 | 1.26 |

3.2. Elemental composition

The elemental composition of the carbon aerogels is presented in Table 2. The aerogel composition changes significantly during pyrolysis. The carbon aerogel after pyrolysis at 1000 °C in nitrogen atmosphere contains only about 20 % of its initial oxygen content. The hydrogen content decreases similarly during pyrolysis. The thermal degradation of cellulose acetate obviously includes the decomposition of oxygen groups and dehydrogenation/aromatisation of the structure. On the contrary, a significantly higher content of nitrogen can be found in the cellulose-acetate-based carbon aerogel (about 3 wt.%) as compared to the organic aerogel (1.8 wt.%). Consequently, nitrogen is at least partly preserved during pyrolysis. The oxidation of the carbon aerogel with hydrogen peroxide leads to the incorporation of an additional 5 wt.% of oxygen, i.e. doubling the O content of the initial carbon. Co-pyrolysis of the carbon aerogel with melamine more than doubles the nitrogen content of the initial carbon aerogel sample.

Table 2. Elemental composition of the cellulose-acetate-based organic aerogel, untreated carbon aerogels (CA), and modified carbon aerogels (CA-OX, CA-M)

| Sample | Elemental composition (wt. %) | | | |
|-----------------|-------------------------------|------|------|-------|
| | C | H | N | O |
| Organic Aerogel | 52.7* | 5.5* | 1.8* | 39.9* |
| CA | 91.05 | 0.85 | 3.04 | 5.06 |
| CA-OX | 86.33 | 0.92 | 3.13 | 9.62 |
| CA-M | 87.08 | 1.1 | 6.71 | 5.11 |

*value calculated from reactant concentration in the sol

3.3. Acid/base properties of the surface

Porous carbons possessing a surface featuring a majority of acidic functional groups can be distinguished from carbons featuring a majority of basic functional groups on its surface. Hence, methods like pH_{PZC} measurement and mass titration are very useful to monitor the surface chemistry. Results presented in Table 2 indicate that carbon aerogel CA displays a basic character, with the concentration of the basic groups fairly exceeding the amount of the acidic groups.

The results of the acid/base titrations show that oxidation in H_2O_2 as well as co-pyrolysis with melamine increases the density of surface functional groups. As expected, the oxidation by hydrogen peroxide increases the quantity of acidic groups on the carbon surface. Meanwhile the density of the basic groups diminishes considerably during oxidation. These modifications are reflected by a slight decrease in the pH_{PZC} value.

The basicity of the carbon treated with melamine is only slightly lower than in case of the initial carbon aerogel CA. This is surprising, as the nitrogen content is twice as high in melamine treated samples. Moreover, some acidic groups are formed, possibly due to oxidation reactions taking place after the nitrogen introduction.

Table 3. Acid-base properties of the functionalised carbon aerogels

| Sample | Acidic groups (mmol/g) | Basic groups (mmol/g) | Acidic groups+basic groups (mmol/g) | pH_{pzc} |
|--------|---------------------------|--------------------------|--|--------------------------|
| CA | 0.138 | 0.496 | 0.634 | 7.13 |
| CA-OX | 0.574 | 0.330 | 0.904 | 6.41 |
| CA-M | 0.233 | 0.410 | 0.643 | 7.08 |

3.4. Electrochemical performance

Cyclic voltammograms for all carbon aerogels are represented in Figure 1. Evidently, the oxidized carbon CA-OX features by far the highest capacitance, while the nitrogen rich sample, CA-M, has obviously the lowest capacitance. The voltammograms of the modified carbons show no evident signs of pseudocapacitive behavior, i.e. peaks due to redox reactions. On the contrary, all three carbons produce similarly shaped voltammograms. Nonetheless, the slopes of the cyclic voltammograms hint at a lower resistance for CA-OX, and a higher resistance for CA-M.

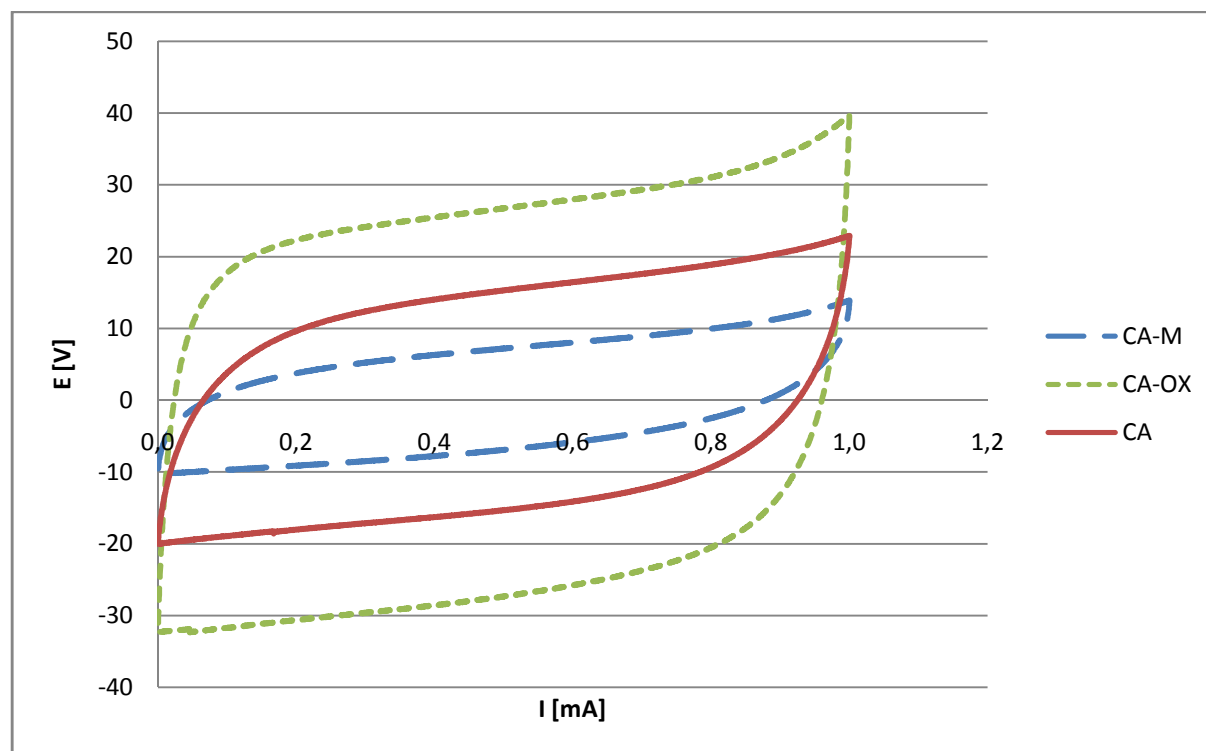


Figure 1. Cyclic voltammograms of carbon aerogels CA, CA-OX, and CA-M at 20 mV/s

Characteristic values for EDLC performance can be found in Table 4. As already indicated by the cyclic voltammograms, CA-OX does not only have the highest capacitance for the particular test assembly, but also the highest volumetric and specific capacitance. At the same time, the equivalent series resistance of CA-OX amounts to only one-fifth of that of CA-M. It is therefore not surprising, that the oxidized sample has also a better performance in terms of specific energy and specific power. What is quite surprising, is the electrochemical performance of CA-M in comparison to the EDLC performance of the initial carbon aerogel. The specific capacitance of CA-M is only half the specific capacitance of CA, while its resistance is about twice as high. This observation does not bear out results from various other studies, stating that high nitrogen content introduces pseudocapacitive behaviour and thus contributes to an enhanced capacitance [8, 9, 10]. More specifically, carbon material enriched in nitrogen by co-pyrolysis with melamine [10] was found to have an enhanced EDLC capacitance. Seredych et al. [10] suggested correlations between the quantity of basic groups and increased capacitance, but not between acid groups and capacitance.

In our case, CA-M features a higher density of surface functional groups on the whole, but less basic groups than CA. Hence, CA-M is less basic than CA. This difference in surface chemistry might partly explain the differences in electrochemical performance between CA and CA-M, according to [10].

CA-OX, on the contrary, features a much higher density of acidic groups than CA, but less basic groups. Therefore, CA-OX is much more acid than CA and CA-M. Nonetheless, the capacitive behaviour of CA-OX is superior to those of CA and CA-M. Thus, at least certain types of acidic oxygen-containing functional groups seem add to capacitance.

Table 4. Electrochemical performance of carbon if used as EDLC electrode, in terms of EDLC capacitance C_{EDLC} , volumetric capacitance C_{vol} , specific capacitance C_{spec} , equivalent series resistance **ESR**, specific energy E_{spec} , specific power P_{spec} , and time constant τ

| | C_{EDLC} (F) | C_{vol} (F/cm ³) | C_{spec} (F/g _{carbone}) | ESR (Ω) | E_{spec} (Wh/kg _{carbone}) | P_{spec} (W/kg _{carbone}) | τ (s/g _{carbone}) |
|-------|-------------------|-----------------------------------|---|----------------------------|---|--|-------------------------------------|
| CA | 0,7 | 21,8 | 33,6 | 0,6 | 1,17 | 4638 | 21 |
| CA-OX | 1,2 | 41,2 | 67,0 | 0,2 | 2,33 | 12775 | 16 |
| CA-M | 0,3 | 10,1 | 17,6 | 1,0 | 0,61 | 3215 | 18 |

*all calculations for IV operating potential, $C_{specific}$ and C_{EDLC} from cyclic voltammetry at 20 mV/s, ESR from galvanostatic cycling at $I = \pm 20$ mA

4. Conclusion

Oxidation of the carbon aerogel in H₂O₂ solution results in an increased oxygen content. Oxygen-containing acidic functional groups are created on the carbon surface, while the quantity of basic functional groups decreases. Consequently, the carbon general acidity increases. Electrochemical analysis of CA-OX in the form of EDLC electrodes features a significantly increased capacitance and reduced resistance in comparison to the initial carbon material CA. High capacitance is suspected to be a product of pseudocapacitive redox reactions between the electrolyte and acidic oxygen-containing surface groups.

Co-pyrolysis of the carbon aerogel with melamine results in the augmentation of the carbon total nitrogen content. Yet, the carbon basicity is not increased, as would rather be expected. In addition, the quantity of basic surface groups decreases slightly, while some acidic groups are created. Further, analysis of CA-M if used as EDLC electrode reveals a poor electrochemical performance. Contrary to expectations, pseudocapacitance enhancing redox reactions do not seem to take place. Capacitance and electrochemical performances lower than for the initial carbon aerogel may partly be due to the slight morphological differences between the un-treated cellulose-acetate-based carbon aerogel CA and the melamine-treated aerogel CA-M (i.e. lower specific surface area s_{BET} and lower porous volumes for CA-M). Also, pseudocapacitive surface functional groups already present in the initial carbon aerogel might have been transformed into functional groups not contributing to capacitance by treatment in melamine.

Obviously, the presence of oxygen atoms enhances the electrochemical performance of CA-OX, while the presence of a non-negligible quantity of nitrogen atoms in sample CA-M does not enhance its capacitance. An augmentation of (pseudo-)capacitance by introducing heteroatoms is evidently feasible. However, the mere presence of heteratoms is not satisfying. We suppose, that only certain types of surface functional groups are beneficial for augmenting capacitance.

Understanding the influence of both the carbon composition and the surface chemistry on the electrochemical performance remains a key objective in EDLC research. Therefore, we focus on identifying the role of different surface groups on capacitive and pseudocapacitive behaviour of carbon material for EDLC electrodes. Results presented in this abstract are only first results of a more comprehensive study on cellulose-acetate-based carbon aerogels modified by different methods (oxidation and/or nitrogen introduction). In the scope of this study, we will also carry out additional analysis of the surface chemistry (e.g. by FTIR and XPS).

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